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Possible methods for biodiesel production

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Abstract

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages. In this work it is made a review of the alternative technological methods that could be used to produce this fuel. Different studies have been carried out using different oils as raw material, different alcohol (methanol, ethanol, buthanol) as well as different catalysts, homogeneous ones such as sodium hydroxide, potassium hydroxide, sulfuric acid and supercritical fluids, and heterogeneous ones such as lipases. In this work advantages and disadvantages of technologies are listed and for all of them a kinetics model is introduced.

Keywords: Biodiesel productions methods; Review

Contents

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1. Introduction

Due to the increase in the price of the petroleum and the environmental concerns about pollution coming from the car gases, biodiesel is becoming a developing area of high concern. There are different ways of production, with different kinds of raw materials: refine, crude or frying oils. Also there are different types of catalyst, basic ones such as sodium or potassium hydroxides, acids such as sulfuric acid, ion exchange resins, lipases and supercritical fluids.

One of the advantages of this fuel is that the raw materials used to produce it are natural and renewable. All these types of oils come from vegetables or animal fat, making it biodegradable and nontoxic. The typical chemical properties of vegetable oils are given in Table 1 [1].

A typical composition of the fatty acid is given in Table 2 [1].

Some fuel properties are shown in Table 3 [2].

A scheme of the flow chart of the process is given in Fig. 1 [3].

Table 1
Fatty acid composition

Vegetable oil	Fatty acid composition % by weight									Acid value	Phos (ppm)	Peroxide value
	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3			
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48	0.11	7	18.4
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00	0.07	8	64.8
Crambe	20.7	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85	0.36	12	26.5
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93	0.20	9	82.7
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.30	8.23	1.14	18	30.2
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31	0.20	32	44.5
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00	0.15	15	10.7

Table 2
Oil composition

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	1.4	2.8	19.2
Palmitic	10.2	20.1	42.8	23.6	23.3	9.8
Stearic	3.7	2.6	4.5	14.2	19.4	3.0
Oleic	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic	8.6	0.6	0.2	0.4	0.9	0.0

Table 3
Properties of the vegetable oils

Vegetable oil	Kinematics viscosity (mm^2/s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Peanut	4.9	54	5	—	176	0.883	33.6
Soya bean	4.5	45	1	−7	178	0.885	33.5
Babassu	3.6	63	4	—	127	0.875	31.8
Palm	5.7	62	13	—	164	0.880	33.5
Sunflower	4.6	49	1	—	183	0.860	33.5
Tallow	—	—	12	9	96	—	—
Diesel	3.06	50	—	−16	76	0.855	43.8
20% biodiesel blend	3.2	51	—	−16	128	0.859	43.2

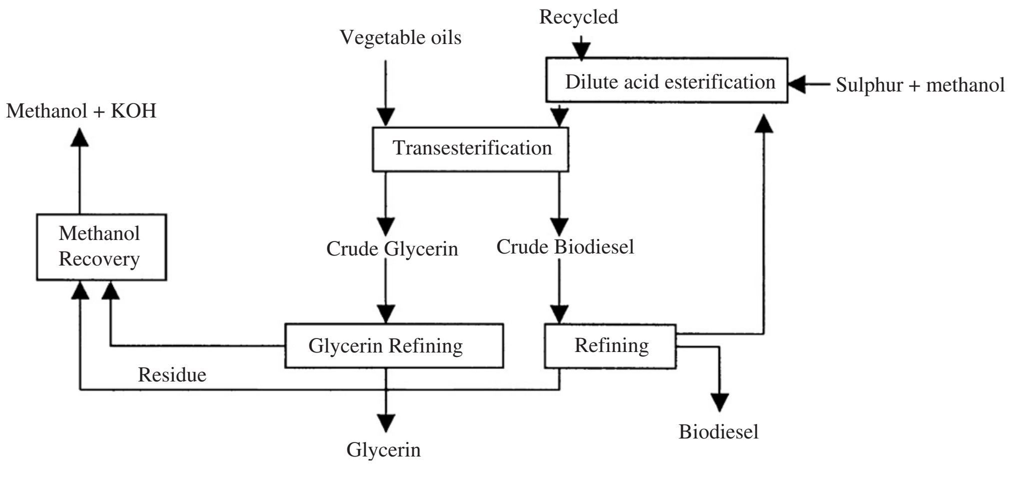


Fig. 1. Basic scheme for Biodiesel production.

2. Transesterification of vegetables oils

In the transesterification [4] of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerin. To make it possible, a catalyst is added to the reaction.

$$\begin{array}{lcccccc} CH_2\text{-}OOC\text{-}R_1 & & & & R_1\text{-}COO\text{-}R' & & CH_2\text{-}OH \\ | & & & \text{Catalyst} & & & | \\ CH\text{-}OOC\text{-}R_2 & + & 3R'OH & \leftrightarrow & R_2\text{-}COO\text{-}R' & + & CH\text{-}OH \\ | & & & & & & | \\ CH_2\text{-}OOC\text{-}R_3 & & & & R_3\text{-}COO\text{-}R' & & CH_2\text{-}OH \\ & & & & & & \\ \text{Glycerides} & & \text{Alcohol} & & \text{Esters} & & \text{Glycerin} \end{array} \quad (1)$$

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, from diglyceride monoglyceride is produced and in the last step, from monoglycerides glycerin is obtained. In all these reactions esters are produced. The stecheometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product:

$$\begin{aligned}
&\text{Triglycerides (TG)} + \text{R}'\text{OH} \underset{k_2}{\overset{k_1}{\leftrightarrow}} \text{Diglycerides (DG)} + \text{R}'\text{COOR}_1,\\
&\text{Diglycerides (DG)} + \text{R}'\text{OH} \underset{k_4}{\overset{k_3}{\leftrightarrow}} \text{Monoglycerides (MG)} + \text{R}'\text{COOR}_2,\\
&\text{Monoglycerides (MG)} + \text{R}'\text{OH} \underset{k_6}{\overset{k_5}{\leftrightarrow}} \text{Glycerin (GL)} + \text{R}'\text{COOR}_3.
\end{aligned} \tag{2}$$

2.1. Process variables

The most relevant variables that this kind of operation are the following:

- Reaction temperature
- Ratio of alcohol to vegetable oil
- Amount of catalyst
- Mixing intensity (RPM)
- Raw oils used
- Catalyst

3. Alkali catalyst

For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol as well as any kind of oils, refine, crude or frying. In this process it is better to produce the Alcoxy before the reaction to obtain a better global efficiency. The alcoxi reaction is

$$\text{R}-\text{CH}_2\text{OH} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{R}-\text{CH}_2\text{ONa}. \tag{3}$$

The alcohol–oil molar ratio that should be used varies from $N = 1{:}1$–$6{:}1$. However $N = 6{:}1$ is the most used ratio giving an important conversion for the alkali catalyst without using a great amount of alcohol. The types of alcohol are usually methanol and ethanol. The last one has fewer safety problems because it is less toxic.

The oils used could come from any vegetable, e.g., corn, canola, peanut, sunflower, soybean, olive, palm, palm kernel. As you may see there are quite a few sources that can be used as raw material and all of them are equally relevant only consideration is in the choice is which has lower price on the market.

The amount of catalyst that should be added to the reactor varies from 0.5% to 1% w/w [3,5], but some authors prefer advice any values between 0.005% and 0.35% w/w [1] should be used.

The last but not least important variable is the reaction temperature. The standard value for the reaction to take place is 60 °C, but depending on the type of catalyst different

temperatures will give different degrees of conversion, and for that reason the temperature range should be from 25 to 120 °C [1–3,6–10].

The reason why there is a great interest in the alkali process is it is more efficient and less corrosive than the acid process, making it a preferred catalyst to be used in industries.

Kinetics studies have been made by Freedman [8], Noureddini and Zhu [9] and Darnoko and Cheryan [11].

The general form of the governing set of differential equations characterizing the stepwise reaction involved in the transesterification of triglycerides is the following:

$$\begin{aligned}
\frac{d[TG]}{dt} &= -k_1[TG][A] + k_2[DG][A] - k_7[TG][A]^3 + k_8[A][GL]^3,\\
\frac{d[DG]}{dt} &= k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E],\\
\frac{d[MG]}{dt} &= k_3[DG][A] - k_4[MG][E] - k_5[MG][A] + k_6[E][GL],\\
\frac{d[TG]}{dt} &= k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E]\\
&\quad + k_5[MG][A] - k_6[GL][E] + k_7[TG][A]^3 - k_8[E]^3[GL],\\
\frac{d[TG]}{dt} &= k_5[ML][A] - k_6[GL][E] + k_7[TG][A]^3 - k_8[GL][E]^3,\\
\frac{d[A]}{dt} &= -\frac{d[E]}{dt}.
\end{aligned} \tag{4}$$

Note that A is alcohol concentration and E denotes ester concentration. Kinetics parameter was estimated using the equation

$$k(T) = AT^n \exp^{-E/RT}. \tag{5}$$

For this kinetics, Noureddini et al. [8] for 50 °C suggested to use values of k given in Table 4.

The limits of this technology are due to the sensitivity that this process has to purity of reactants, to the fatty acid, as well as to the water concentration of the sample.

If you have too much water you run the risk of making some soap instead of the desired product. If soap is the endproduct, a consummation of the reactive will take place and the

Table 4
Values of the kinetics parameter

Kinetics parameter	Value
k_1	0.049
k_2	0.102
k_3	0.218
k_4	1.280
k_5	0.239
k_6	0.007
k_7	7.84E−5
k_8	1.58E−5

formation of an emulsion, that makes downstream recovery and purification very difficult and expensive occurs.

A normal amount of free fatty acid on the waste cooking oils is about 2% w/w. If you have an amount this big, Lepper and Friesenhagen recommend a pretreatment via esterification with alcohol but with sulfuric acid. After this, we have to continue with the normal alkali process.

4. Acid catalyst

This way of production is the second conventional way of making the biodiesel. The idea is to use the triglycerides with alcohol and instead of a base to use an acid—the most commonly used is sulfuric acid [7,9,12] and some authors prefer sulfonic acid [13]. This type of catalyst gives very high yield in esters but the reaction is very slow, requiring almost always more than one day to finish. Freedman and Pryde [9] get the desirable product with 1 mol% of sulfuric acid with a molar ratio of 30:1 at 65 °C and they get 99% of conversion in 50 h, while the butanolysis will need 117 °C and the ethanolysis 78 °C but the times should be 3 and 18 h, respectively.

As in the alkali reaction, if an excess of alcohol is used in the experiment then better conversion of triglycerides is obtained, but recovering glycerol becomes more difficult and that is why optimal relation between alcohol and raw material has should be determined experimentally considering each process as a new problem.

The possible operation condition is, usually, molar ratio 30:1. The type of alcohol, as well as the oils, is the same as the one that can be used in alkali catalyst reaction. The amount of catalyst supposed to be added to the reactor varies from 0.5 to 1 mol%. The typical value is 1%, but some authors have used 3.5 mol% [6,14].

The temperature range varies from 55 to 80 °C. The acid transesterification is a great way to make biodiesel if the sample has relatively high free fatty acid content. In general, a 1 mol% of sulfuric acid is a good amount for a final conversion of 99% in a time around 50 h.

A kinetics modeling for soybean oil has been made by Freedman [9]. He makes the kinetics with BuOH using a molar relation of 30:1 with 1% H_2SO_4 at five different temperatures. In their work, they expect the reaction to follow a pseudo first-order kinetics. The results that they obtained are shown in the following graphic; performed at 117 °C (Fig. 2).

5. Lipase as catalyst

Lipases are enzymes used to catalyze some reaction such as hydrolysis of glycerol, alcoholysis and acidolysis, but it has been discovered that they can be used as catalyst for tranesterification and esterification reactions too. Biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure are the desired properties in agricultural and medical applications.

The extra cellular and the intracellular lipases are also able to catalyze the transesterification of triglycerides effectively.

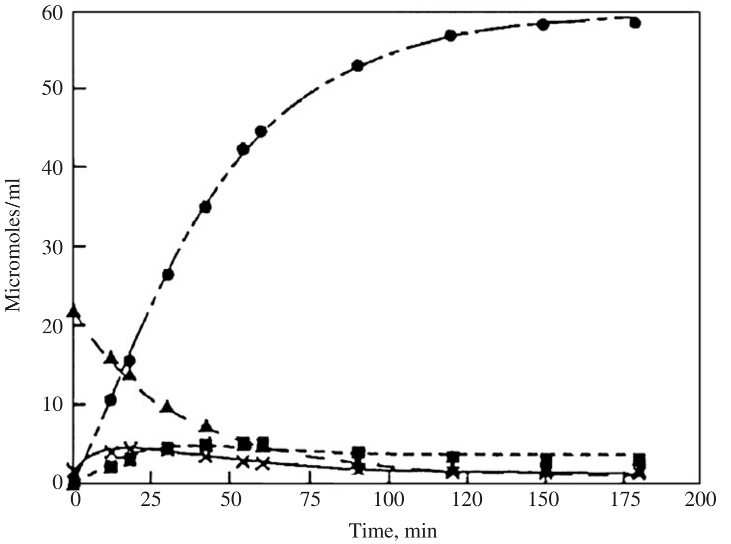


Fig. 2. Change of components concentration with time. (●) Soybean butyl esters, (▲) soybean oils, (x) diglycerides, (■) monoglycerides.

5.1. The advantages of using lipases

1. Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if you keep the reactive flow,
2. Use of enzymes in reactors allows use of high concentration of them and that makes for a longer activation of the lipases,
3. A bigger thermal stability of the enzyme due to the native state,
4. Immobilization of lipase could protect it from the solvent that could be used in the reaction and that will prevent all the enzyme particles getting together,
5. Separation of product will be easier using this catalyst [15].

5.2. Some disadvantages

1. You can lose some initial activity due to volume of the oil molecule.
2. Number of support enzyme is not uniform.
3. Biocatalyst is more expensive that the natural enzyme.

Nelson [16] has investigated the use of lipases with short chain alcohols to give alkyl esters. He obtained a good transesterification to ester using M. Miehi as catalyst.

Shimada [17] worked on production of biodiesel using lipase but waste oil as raw material. They started the enzymatic production using normal oil and methanol and the first interesting result is that if the amount of the molar relationship is larger than 0.5, the product becomes insoluble of alcohol. This fact reduces the activation with lipase (Fig. 3).

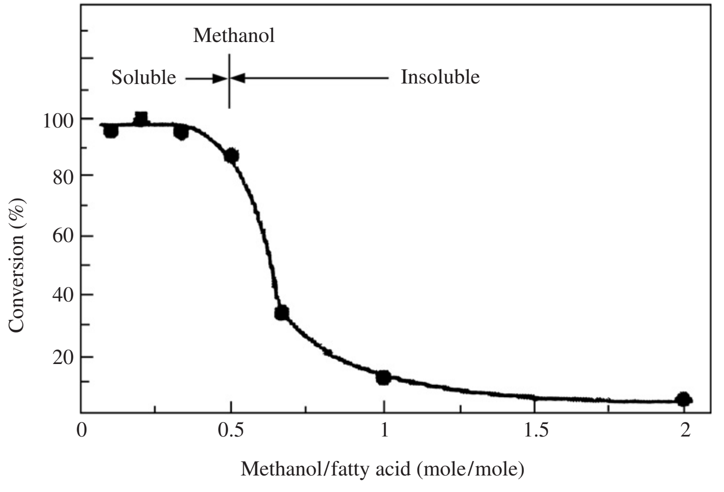


Fig. 3. Methanolysis of vegetable oil with different amounts of MeOH using immobilized *C. antarctica* lipase (Novozym 435; Novozymes, Bagsvaerd, Denmark).

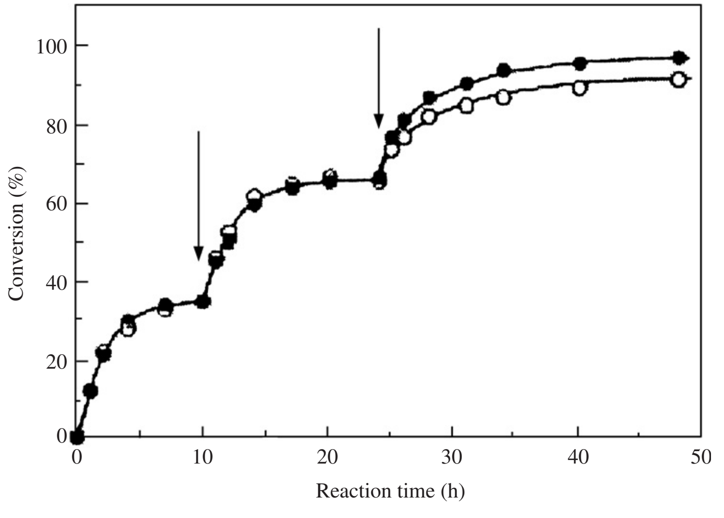


Fig. 4. Three-step batch methanolyses of waste oil.

Nelson et al. [16] and Shimada et al. [17] use one type of reaction that needs 1/3 of the alcohol to be fed at the beginning, 1/3 10 h after and the other third later than 24 h from the start of reaction. A normal graphic obtained is given in Fig. 4.

Lipase esterification is a viable method for the production of alkyl esters from animal fat or vegetable oils. The basic scheme for this mechanic is given in Fig. 5 [18].

Note that E stands for enzyme, Es for ester, Al for alcohol and Ac for acid.

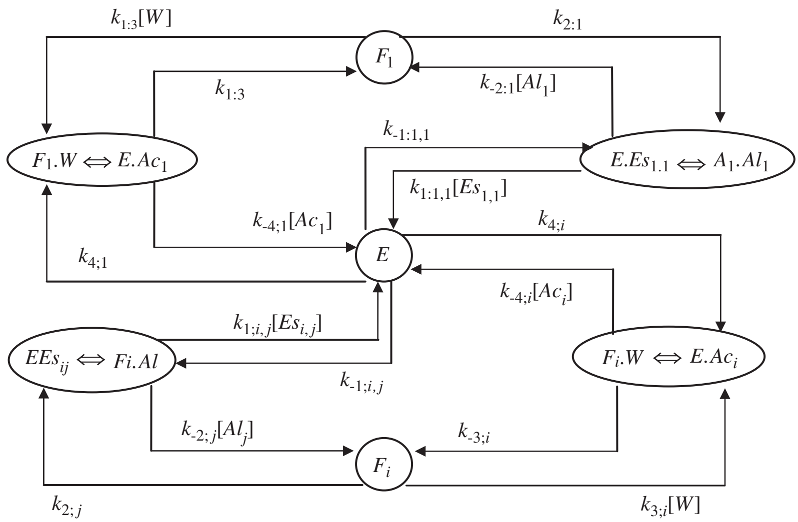


Fig. 5. King–Altman's basic scheme associated to the lipase reaction kinetics mechanism.

The rate expression for a Ping Pong Bi Bi mechanism is

$$r_{m,n} = \frac{\begin{array}{l}(k_{1;m,n}k_{2;n}k_{3;m}k_{4;m}[\mathrm{Es}_{m,n}][W] - k_{-1;m,n}k_{-2;n}k_{-3;m}k_{-4;m}[\mathrm{Al}_n][\mathrm{Ac}_m]) \\ *[E]_{\mathrm{tot}} \prod_{j=1}^{J}\prod_{i=1}^{I} \frac{(k_{-2;j}k_{-1;i,j}(k_{-3;i}+k_{4;i})[\mathrm{Al}_j]+k_{3;i}k_{4;i}(k_{-1;i,j}+k_{2;j})[W])}{(k_{-2;n}k_{-1;m,n}(k_{-3;m}+k_{4;m})[\mathrm{Al}_n]+k_{3;m}k_{4;m}(k_{-1;m,n}+k_{2;n})[W])}\end{array}}{\begin{array}{l}\sum_{n=1}^{J}\sum_{m=1}^{I}\left\{ k_{-2;n}k_{-1;m,n}(k_{-3;m}+k_{4;m})[\mathrm{Al}_n] + k_{3;m}k_{4;m}(k_{-1;m,n}+k_{2;n})[W] \right. \\ +k_{-2;n}k_{1;m,n}(k_{-3;m}+k_{4;m})[\mathrm{Es}_{m,n}][Al_n] + k_{1;m,n}k_{3;m}k_{4;m}[\mathrm{Es}_{m,n}][W] \\ +k_{-4;m}k_{-3;m}k_{-2;n}[\mathrm{Al}_n][\mathrm{Ac}_m] + k_{1;m,n}k_{2;n}(k_{-3;m}+k_{4;m})[\mathrm{Es}_{m,n}] \\ +k_{-3;m}k_{-4;m}(k_{-1;m,n}+k_{2;n})[\mathrm{Ac}_m] + k_{-4;m}k_{3;m}(k_{-1;m,n}+k_{2;n})[W][\mathrm{Ac}_m] \\ +k_{1;m,n}k_{2;n}k_{3;m}[\mathrm{Es}_{m.n}][W] + k_{-4;m}k_{-2;n}k_{-1;m,n}[\mathrm{Al}_n][\mathrm{Ac}_m]) \\ \left. *\prod_{j=1}^{J}\prod_{i=1}^{I} \frac{(k_{-2;j}k_{-1;i,j}(k_{-3;i}+k_{4;i})[\mathrm{Al}_j]+k_{3;i}k_{4;i}(k_{-1;i,j}+k_{2;j})[W])}{(k_{-2;n}k_{-1;m,n}(k_{-3;m}+k_{4;m})[\mathrm{Al}_n]+k_{3;m}k_{4;m}(k_{-1;m,n}+k_{2;n})[W])} \right\}\end{array}} \quad (6)$$

where $m = 1, 2, \ldots, I$; $n = 1, 2, \ldots, J$.

6. Use of supercritical alcohols

Although this is a new topic becoming and more relevant [19,20], there is an uncertainty regarding whether tranesterification or alkyl esterification is a better way of production and which one has a faster reaction rate. Some results obtained by Kusdiana et al. [20] are given in Fig. 6.

In alkyl esterification, under the same conditions as the previous one, the results obtained are given in Fig. 7.

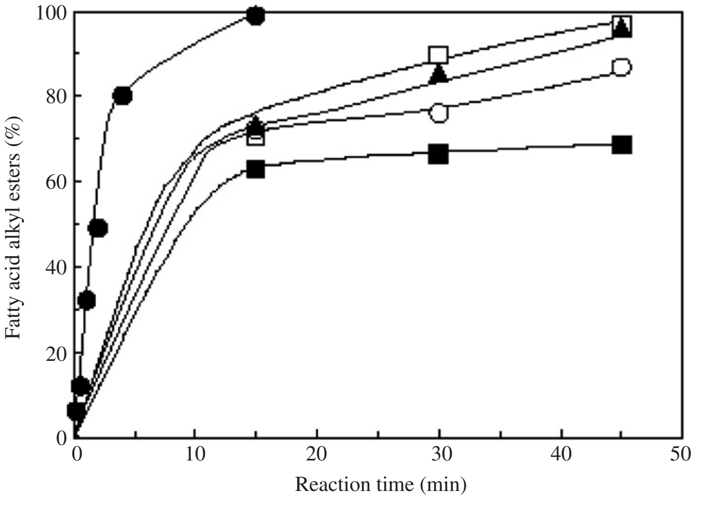


Fig. 6. Relation for (●) methanol, (□) ethanol, (▲) 1-propanol, (○) 1-butanol, (■) 1-octanol.

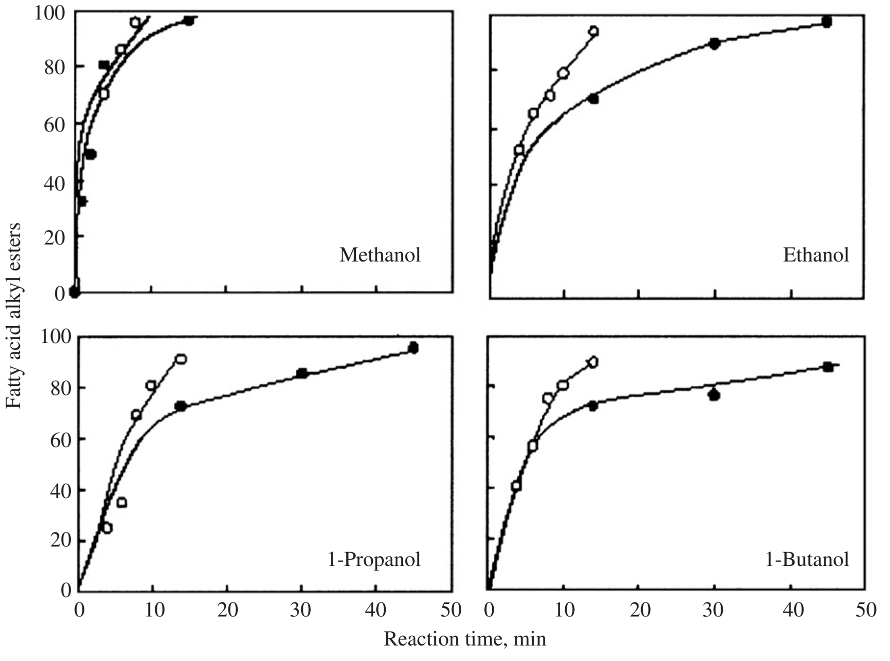


Fig. 7. Relation for (○) is for the fatty acid and (●) for the triglycerides.

It is easy to see from the works of Warabi and Kusdiana and their coworkers [19,20] that alkyl esterification has a higher reaction rate compare to transesterification. This shows that the free fatty acid that may be present in oils will get completely transformed into the fuel under transesterification.

A kinetics study has been carried out by Kusdiana and Saka [20]. They have proposed a first-order kinetics:

$$\ln\frac{[\mathrm{uME}, t]}{[\mathrm{uME}, 0]} = kt, \tag{7}$$

where k is the kinetic constant and uME is the content of the species excluding esters and glycerin. The later is evaluated at a time t and at the start of reaction.

7. Conclusions

For the alkyl catalyzed reaction, it was found that this is a very good process of production with relatively high conversion. The kinetics procedure of Freedman et al. [9] follows a normal pseudo first-order kinetics, as well as acid-catalyzed kinetics.

Noureddini et al. [8] have obtained good transesterification kinetics for acid catalyzed reaction of soybean oils. The conversion is about 60%, not very high compared to those of some other authors. This could be so because of differences in the time at which they have done their experiments, temperature, alcohol and raw oil used. However, there is a possible production process.

In the case where supercritical alcohol was used, it was demonstrated that one gets a higher reaction rate for esterification than for transesterification. Another advantage of this process is that the free fatty acid will be changed completely into esters.

The use of lipase is a great viable method for production of ester from different sources of oil or grease. Research on this topic is still in progress due to the enzyme flexibility and adaptability to new process.

A summary of the advantages and disadvantages of each technological possibility to produce biodiesel could be found in Table 5.

Table 5
Comparison of the different technologies to produce Biodiesel

Variable	Alkali catalysis	Lipase catalysis	Supercritical alcohol	Acid catalysis
Reaction temperature (°C)	60–70	30–40	239–385	55–80
Free fatty acid in raw materials	Saponified products	Methyl esters	Esters	Esters
Water in raw materials	Interference with reaction	No influence		Interference with reaction
Yield of methyl esters	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Easy		Difficult
Purification of methyl esters	Repeated washing	None		Repeated washing
Production cost of catalyst	Cheap	Relatively expensive	Medium	Cheap

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